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NATIONAL BUREAU OF STANDARDS REPORT

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Quarterly Report

Electrodeposition of Molybdenum

April 1 - June 30, 1953

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

U. S. DEPARTMENT OF COMMERCE
Charles Sawyer, *Secretary*

NATIONAL BUREAU OF STANDARDS
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THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section is engaged in specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant reports and publications, appears on the inside of the back cover of this report.

Electricity. Resistance Measurements. Inductance and Capacitance. Electrical Instruments. Magnetic Measurements. Applied Electricity. Electrochemistry.

Optics and Metrology. Photometry and Colorimetry. Optical Instruments. Photographic Technology. Length. Gage.

Heat and Power. Temperature Measurements. Thermodynamics. Cryogenics. Engines and Lubrication. Engine Fuels. Cryogenic Engineering.

Atomic and Radiation Physics. Spectroscopy. Radiometry. Mass Spectrometry. Solid State Physics. Electron Physics. Atomic Physics. Neutron Measurements. Infrared Spectroscopy. Nuclear Physics. Radioactivity. X-Rays. Betatron. Nucleonic Instrumentation. Radiological Equipment. Atomic Energy Commission Instruments Branch.

Chemistry. Organic Coatings. Surface Chemistry. Organic Chemistry. Analytical Chemistry. Inorganic Chemistry. Electrodeposition. Gas Chemistry. Physical Chemistry. Thermochemistry. Spectrochemistry. Pure Substances.

Mechanics. Sound. Mechanical Instruments. Aerodynamics. Engineering Mechanics. Hydraulics. Mass. Capacity, Density, and Fluid Meters.

Organic and Fibrous Materials. Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Organic Plastics. Dental Research.

Metallurgy. Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion.

Mineral Products. Porcelain and Pottery. Glass. Refractories. Enameled Metals. Concreting Materials. Constitution and Microstructure. Chemistry of Mineral Products.

Building Technology. Structural Engineering. Fire Protection. Heating and Air Conditioning. Floor, Roof, and Wall Coverings. Codes and Specifications.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Machine Development.

Electronics. Engineering Electronics. Electron Tubes. Electronic Computers. Electronic Instrumentation.

Radio Propagation. Upper Atmosphere Research. Ionospheric Research. Regular Propagation Services. Frequency Utilization Research. Tropospheric Propagation Research. High Frequency Standards. Microwave Standards.

Ordnance Development.
Electromechanical Ordnance.
Electronic Ordnance.
These three divisions are engaged in a broad program of research and development in advanced ordnance. Activities include basic and applied research, engineering, pilot production, field testing, and evaluation of a wide variety of ordnance matériel. Special skills and facilities of other NBS divisions also contribute to this program. The activity is sponsored by the Department of Defense.

Missile Development. Missile research and development: engineering, dynamics, intelligence, instrumentation, evaluation. Combustion in jet engines. These activities are sponsored by the Department of Defense.

● Office of Basic Instrumentation

● Office of Weights and Measures.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT | NBS REPORT

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Electrodeposition of Molybdenum

by

S. Senderoff, L. Goslee, W. Reid, Jr., and A. Brenner

Sponsored by
Springfield Armory
Watertown Arsenal

Electrodeposition of Molybdenum

During this quarter the work was concentrated on electrodeposition from fused electrolytes.

Attempts to refine the grain-size and improve the properties of the molybdenum plate by alloy addition agents were continued.

Ferrous chloride was added to the molybdenum-plating solution in concentrations of 0.75% and 3.6% by weight. At 3 amp/dm^2 and 600°C, plates of almost 0.001" thickness were obtained which appeared to be smoother than those obtained previously and which proved to be much finer-grained, and less porous when examined metallographically. However, the deposits were quite brittle and were produced at extremely low current efficiency. With the bath containing 0.75% $FeCl_2$, the efficiency was 16%, and with the bath containing 3.6% $FeCl_2$, the efficiency was 11%. The deposits contained 1.0% to 1.1% iron.

Various attempts were made to increase the efficiency by variations in current density but these were unsuccessful. While it is probable that the addition of iron has had some slightly beneficial effect on the properties of the deposit, the drastic reduction in current efficiency which results from its use is very undesirable. With the efficiencies attainable it takes four hours to plate 0.001". The reduction in efficiency is believed to result from oxidation of the ferrous to ferric iron at the anode followed by reduction again to the ferrous state at the cathode. With such cycling, even small amounts of iron in the bath could seriously reduce the efficiency.

Additions of cobalt chloride in concentrations of 0.75%, 3.6%, and 7.0% by weight were made to the

molybdenum plating solution. These plates also showed better structure than those produced without addition agents, but on standing overnight they cracked. It was observed that the molybdenum cracked away from the nickel undercoat and split as it did so. The addition of cobalt chloride seriously raises the stress in the molybdenum plate. Analysis of the deposits from all baths showed no detectable cobalt in the plate, indicating that there was probably less than 0.1% cobalt in the plate.

The high stress produced, together with the absence of any appreciable cobalt in the deposit, indicates a strong addition agent action not associated with alloying. This may be of some benefit under careful control of composition of the bath and will be investigated further.

In order to determine whether some of the porosity and roughness may be due to gross particles in the solution, a standard molybdenum plating solution was purified and then filtered, while molten, through a porous alundum crucible which had been thoroughly baked in a helium atmosphere. No improvements as a result of the filtration was observed.

Since this is the last report for the contract year a summary of activities for the year is appended.

I. From Fused Salts.

The method for preparation and purification of potassium hexachloromolybdate for use in the molybdenum plating bath was studied and improved.

Of a large number of metals and alloys tested for use as a strike plate on steel, which was subsequently

to be plated with molybdenum, nickel was found to be most satisfactory. Of various thicknesses of nickel for this strike plate, 0.001" was found to give most consistently good results, though 0.0005" may also be satisfactory under certain conditions.

The plating variables of current density, rate of cathode agitation, purity of salts, composition of bath, and treatments for the nickel undercoating were systematically studied in an attempt to improve the deposit, but it was decided insufficient improvement was obtained, even at optimum conditions, to merit the study of further small variations in these conditions. Plates up to about 0.001" in thickness are fairly smooth, but mechanically weak due to a coarse-grained structure. Above 0.001" they are rough and brittle.

Alloying addition agents at various concentration levels and over a range of current densities were tried in order to improve the properties of the deposit.

Thus far, nickel, cobalt, and iron have been tried. In some cases the grain-structure of the deposits was improved but other undesirable properties such as low efficiency and high stress were observed to result from the addition of these metals.

Work with alloying addition agents is continuing and studies of colloidal addition agents will be undertaken.

II. Organic Solvents.

The attempts to deposit molybdenum from organic solvents has not been successful but all possibilities have not been exhausted. A large amount of time was spent

on the attempts to produce a borohydride derivative of molybdenum, since aluminum and beryllium can be deposited from such compounds. A pure molybdenum borohydride could not be prepared. A reactive black compound containing molybdenum, boron, and chlorine was obtained which was not very soluble in organic solvents and no deposit was obtained by electrolysis of such solutions.

The electrolysis of molybdenum halides in various amines, in which they are quite soluble, produced in some instances a flash deposit which, however, could not be built up and therefore was not further examined.

The last phase of the work was concerned with the use of a certain class of active sodium compounds formed by adding sodium to aromatic hydrocarbons. These solutions in organic solvents conduct and deposits were obtained which contained molybdenum, probably alloyed with sodium. Further work will be done with these systems.

Another direction for future work will be in the preparation of molybdenum derivatives of cyclopentadiene. No pure organometallic compounds of molybdenum were isolated prior to the recently reported discovery of the stable organometallic derivatives of cyclopentadiene. The preparation of the molybdenum compound is now under way, and studies will be made of its electrolytic behavior.

III. Deposition of Metals on Titanium.

The procedure of using a fluoride etch on titanium as a pretreatment for securing adhesion of

electrodeposits was found to be inadequate. The best results were obtained by the following steps: treat the titanium anodically in a solution of hydrofluoric acid in acetic acid and water; deposit about 0.0001" of copper on the titanium from a cyanide copper bath; heat-treat in argon at 800°C for two minutes to form a diffusion bond; continue the deposition with any other electrodeposit desired.

Probably the best method of obtaining adhesion of other metals to titanium is the procedure developed in connection with the aluminum plating program, in which aluminum is deposited on titanium after an anodic treatment in the bath. The aluminum is then given the zincate treatment in the usual fashion and plated with other metals.

THE NATIONAL BUREAU OF STANDARDS

Functions and Activities

The functions of the National Bureau of Standards are set forth in the Act of Congress, March 3, 1901, as amended by Congress in Public Law 619, 1950. These include the development and maintenance of the national standards of measurement and the provision of means and methods for making measurements consistent with these standards; the determination of physical constants and properties of materials; the development of methods and instruments for testing materials, devices, and structures; advisory services to Government Agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; and the development of standard practices, codes, and specifications. The work includes basic and applied research, development, engineering, instrumentation, testing, evaluation, calibration services and various consultation and information services. A major portion of the Bureau's work is performed for other Government Agencies, particularly the Department of Defense and the Atomic Energy Commission. The scope of activities is suggested by the listing of divisions and sections on the inside of the front cover.

Reports and Publications

The results of the Bureau's work take the form of either actual equipment and devices or published papers and reports. Reports are issued to the sponsoring agency of a particular project or program. Published papers appear either in the Bureau's own series of publications or in the journals of professional and scientific societies. The Bureau itself publishes three monthly periodicals, available from the Government Printing Office: The Journal of Research, which presents complete papers reporting technical investigations; the Technical News Bulletin, which presents summary and preliminary reports on work in progress; and Basic Radio Propagation Predictions, which provides data for determining the best frequencies to use for radio communications throughout the world. There are also five series of nonperiodical publications: The Applied Mathematics Series, Circulars, Handbooks, Building Materials and Structures Reports, and Miscellaneous Publications.

Information on the Bureau's publications can be found in NBS Circular 460, Publications of the National Bureau of Standards ($1.00). Information on calibration services and fees can be found in NBS Circular 483, Testing by the National Bureau of Standards (25 cents). Both are available from the Government Printing Office. Inquiries regarding the Bureau's reports and publications should be addressed to the Office of Scientific Publications, National Bureau of Standards, Washington 25, D. C.